

**Isothermal VLE Measurements for the Binary Mixtures HFC-  
134a+HFC-245fa and HC-600a+HFC-245fa <sup>1</sup>**

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## ABSTRACT

The substitution of CFC-114 in high temperature heat pumps is still far from the solution. Some pure compounds such as HFC-236ea, HFC-236fa, HFC-245fa have been proposed, but it is probable that the best alternative will be given by a binary or ternary mixture including one of these fluids. The experimental data on the thermodynamic properties of these fluids are still scarce and, as refer the mixtures, the evaluation of vapor-liquid equilibrium (VLE) behavior is crucial.

This paper presents the measurement of isothermal VLE  $p$ - $T$ - $x$ - $y$  data of the two binary refrigerant systems HFC-134a + HFC-245fa and HC-600a + HFC-245fa at three temperatures ranging from 293.15 K to 313.15 K. The measurements are performed by means of an apparatus based on the recirculation of vapor into liquid and the gas-chromatographic analysis of the composition. The estimated accuracies of measured data are  $\pm 0.02$  K for temperature,  $\pm 1$  kPa for pressure,  $\pm 0.002$  in mole fraction for liquid composition and  $\pm 0.003$  in mole fraction for vapor composition. The VLE data are correlated with the RKS equation of state in connection with the Huron-Vidal mixing rules, obtaining a very good agreement between the experimental and the calculated data.

KEYWORDS: data, vapour-liquid equilibria, mixture, 1,1,1,3,3-pentafluoropropane, 1,1,1,2-tetrafluoroethane, isobutane.

## 1. INTRODUCTION

Even if a big effort in searching new refrigerants as substitutes for CFCs has been performed in the last decade, not all the questions are solved yet. In particular, no proper substitutes for CFC-114, a high boiling fluid used for high temperature applications such as industrial heat pumps, has been definitively identified, though some fluids such as 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa) and 1,1,1,3,3-pentafluoropropane (HFC-245fa) have been proposed as possible candidates. Anyway, within the synthetic fluids, the most efficient solution will come probably from mixtures of two or more components rather than from pure compounds, as it happens for the substitutes for HCFC-22 and R502.

Within the last years, an extensive research work has been performed by CNR-ITEF to study the properties of mixtures formed by fluorinated derivatives of propane and other HFCs or hydrocarbons. Several VLE measurements were performed to give useful information for the selection of substitutes for CFC-114 but also to extend the knowledge of the thermodynamic behavior of fluoropropanes when mixed with HFCs and hydrocarbons [1-7].

This paper reports on the VLE measurements and data reduction on the binary systems 1,1,1,2-tetrafluoroethane (HFC-134a) + 1,1,1,3,3-pentafluoropropane (HFC-245fa) and isobutane (HC-600a) + HFC-245fa.

## 2. EXPERIMENTAL SECTION

*2.1 Materials.* HFC-245fa, with no impurities detected by gas chromatography using both the flame ionization detector (FID) and the thermal conductivity detector (TCD), was supplied by Allied Signal.

HFC-134a, with no impurities detected by the FID and by the TCD, was supplied by Ausimont.

HC-600a, with 0.1% impurities detected by the FID and by the TCD, was supplied by Aldrich with declared purity higher than 99%.

In order to eliminate the non-condensable gases, each sample underwent several cycles of freezing with liquid nitrogen, evacuation, thawing and ultrasound. The samples were then used with no further purification.

*2.2 Apparatus.* The equilibrium between liquid and vapor phase is reached in a stainless steel cell of about 50 cm<sup>3</sup> capacity. The cell is equipped with a magnetic pump used to recirculate the vapor phase into the liquid one to get faster equilibrium. The VLE cell and the magnetic pump were immersed in a thermostatic water bath of about 100 L capacity.

The temperature in the bath was stabilized at  $\pm 1$  mK throughout the measurements by means of a PID-controlled system governing a heater immersed in the bath. An auxiliary thermostatic bath was used to compensate for the heat produced by the PID-controlled system and to change the level of temperature in the main bath.

Temperature was measured with a 100  $\Omega$  platinum resistance thermometer (ISOTECH 909/100) and the uncertainty in temperature measurement was estimated to be  $\pm 0.02$  K.

Pressure was measured by means of a pressure gauge (RUSKA 6000) with a full scale of 3500 kPa. A differential pressure cell (RUSKA 2413) immersed in the thermostatic bath was used to separate the chemicals from the quartz sensor of the pressure gauge. The uncertainty in the pressure measurement is estimated to be within  $\pm 1$  kPa, including the accuracy of the pressure transducer and the stability of the

pressure during the measurements.

The composition of the vapor and liquid phases was established by gas chromatographic analysis. A gas chromatograph (Hewlett-Packard 6890) was connected on-line to the VLE cell. The response of the detector was carefully calibrated using gravimetrically-prepared mixtures. Considering the reproducibility of gas chromatography, the stability of the composition during the measurements and the uncertainty in calibration, we estimated the accuracy in composition measurements to be within  $\pm 0.002$  in mole fraction of liquid phase and  $\pm 0.003$  in mole fraction of vapor phase.

### 3. RESULTS AND DISCUSSION

The  $P$ ,  $x$ ,  $y$  equilibrium data for the mixtures HFC-134a + HFC-245fa and for the mixtures HC-600a + HFC-245fa, measured at temperatures 293.15 K, 303.15 K and 313.15 K, are presented in Tables 1 and 2, respectively. The vapor and liquid phase saturation boundaries are shown in Figure 1 for the system HFC-134a + HFC-245fa and in Figure 2 for the system HC-600a + HFC-245fa. Throughout the paper,  $x$  and  $y$  indicate the liquid and vapor mole fractions, respectively, while  $P$  stands for the pressure in kPa.

The mixture HFC-134a + HFC-245fa shows an almost ideal behavior. The mixture HC-600a + HFC-245fa shows a big positive deviation from the Raoult's law, with presence of an azeotrope at molar fraction of HC-600a higher than 0.75.

*3.1 Pure compounds vapor pressures.* Comparison of pure compounds experimental vapor pressures with literature data is important to have a more reliable evaluation of the actual accuracy in pressure measurement. For this reason, we compared our data with several data reported in literature [8-21]. In the cases where vapor pressures

reported in literature were not at the same temperature as ours, the vapor pressure was calculated at our experimental temperatures using the vapor pressure equation proposed by the authors [8, 9, 11-14, 20] or, when it was not proposed [16, 17], regressing the data in literature with a Wagner equation in the form shown by Reid et al. [22] and the pure compounds critical parameters taken from [9, 23, 24]. The results are shown in Table 3. There is generally a valid consistency between our data and data in the literature. For R134a deviations were within  $\pm 0.1\%$  in most cases: due to the high number and quality of literature data considered for the comparison, we can be confident on the accuracy of our measurements. Higher percentage deviations were found in the case of HFC-245fa from values taken from Sotani et al. [8]. For HC-600a our data are in good agreement with McLinden [9], while relatively high deviations from the values calculated from Beattie et al. [20] were found.

*3.2 Data reduction.* The VLE data were reduced by means of the the Redlich-Kwong-Soave (RKS) equation of state (Soave [25] and Soave [26]) with the Huron-Vidal (HV) mixing rules (Huron and Vidal [27]) and the relevant Margules equation for excess Gibbs free energy (binary mixtures) (Van Ness and Abbott [28]), on the base of a method developed by Bertucco et al. [29] and already used in Bobbo et al. [4, 6]. The use of Margules equation gives the necessary flexibility to fit the excess Gibbs energy functions obtained by the experimental data: the number of adjustable parameters (2, 4 or 6) can be defined in such a way to get the best fit.

The Margules parameters were fitted by minimization of the following objective function:

$$obf = \sum_{i=1}^{N_p} (\Delta P / P_{\text{exp}})^2$$

where  $N_p$  is the number of isothermal data points considered, and the residuals on pressure are given by:

$$\Delta P / P_{\text{exp}} = \frac{P_{\text{calculated}} - P_{\text{experimental}}}{P_{\text{experimental}}}.$$

The values for the critical properties of the compounds that were used to perform the consistency test are taken from [9, 23, 24].

The diagrams of Figures 3 to 6 show the deviations of pressures and vapor compositions calculated with RKS-HV EOS from experimental data, while Table 4 summarizes the results of the data reduction.

By analyzing the results reported in Table 4 and looking at the diagrams of deviations for pressure, one can see that the bias of pressure is practically zero for all the isotherms and also the absolute average deviation (AAD) in pressure is very small. This indicates the absence of systematic error and a negligible scattering in the pressure representation. The deviation in vapor composition ( $\Delta y = y_{\text{calculated}} - y_{\text{experimental}}$ ) is slightly higher in the case of the HFC-134a+HFC-245fa mixture and with a systematic positive behavior. However, in both cases the deviations are of the same order of the declared experimental error and are small enough for the data and the adopted model to be considered consistent.

#### 4. CONCLUSIONS

This paper dealt with the measurements of VLE for two binary systems formed by the HFC-245fa with HFC-134a and HC-600a respectively. The results show a behavior close to ideality for the system HFC-134a + HFC-245fa, while a big positive deviation from the Raoult's law is observed for the system HC-600a + HFC-245fa, which forms an azeotrope at molar fraction of HC-600a slightly higher than 0.75. These results

confirm the behavior already observed for the fluoropropane HFC-245fa when mixed with the HFC-125 and the hydrocarbon HC-290 [6]. The Redlich-Kwong-Soave equation of state with the Huron-Vidal mixing rules was used for the data reduction and it showed to be very suitable at the representation of experimental VLE for both systems.



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**Table 1.** Vapor-Liquid Equilibrium Data for HFC-134a (1) + HFC-245fa (2) System at  $T = 293.15\text{ K}$ ,  $303.15\text{ K}$  and  $313.15\text{ K}$ .

$T = 293.15\text{ K}$			$T = 303.15\text{ K}$			$T = 313.15\text{ K}$		
$x_{l, exp}$	$y_{l, exp}$	$P_{exp}/\text{kPa}$	$x_{l, exp}$	$y_{l, exp}$	$P_{exp}/\text{kPa}$	$x_{l, exp}$	$y_{l, exp}$	$P_{exp}/\text{kPa}$
0.0000	0.0000	122.8	0.0000	0.0000	179.0	0.0000	0.0000	250.8
0.0640	0.2242	150.5	0.1211	0.3450	246.3	0.1419	0.3633	350.4
0.1836	0.4837	202.3	0.3084	0.6222	349.6	0.2764	0.5637	446.4
0.3375	0.6734	268.5	0.4037	0.7113	403.9	0.4103	0.6963	544.0
0.4473	0.7632	315.3	0.4889	0.7753	452.9	0.5408	0.7931	645.2
0.6140	0.8622	390.7	0.6089	0.8469	523.9	0.6368	0.8503	717.8
0.7205	0.9082	439.5	0.7126	0.8960	586.6	0.6458	0.8535	723.4
0.8565	0.9568	502.7	0.8785	0.9603	690.6	0.7365	0.8969	794.0
0.9717	0.9919	558.2	0.9748	0.9917	753.5	0.8323	0.9376	872.7
1.0000	1.0000	571.3	1.0000	1.0000	769.4	0.9479	0.9817	970.8
						1.0000	1.0000	1014.6

**Table 2.** Vapor-Liquid Equilibrium Data for HC-600a (1) + HFC-245fa (2) System at T = 293.15 K, 303.15 K and 313.15 K.

<i>T = 293.15 K</i>			<i>T = 303.15 K</i>			<i>T = 313.15 K</i>		
$x_{l, exp}$	$y_{l, exp}$	$P_{exp}/\text{kPa}$	$x_{l, exp}$	$y_{l, exp}$	$P_{exp}/\text{kPa}$	$x_{l, exp}$	$y_{l, exp}$	$P_{exp}/\text{kPa}$
0.0000	0.0000	122.8	0.0000	0.0000	179.0	0.0000	0.0000	250.6
0.0390	0.3021	173.1	0.0328	0.2419	231.2	0.0273	0.1738	302.3
0.0977	0.4804	226.7	0.0721	0.3922	283.7	0.0685	0.3305	364.2
0.1899	0.5918	274.6	0.1490	0.5223	345.9	0.1400	0.4688	442.4
0.3092	0.6532	305.4	0.2672	0.6047	394.5	0.2012	0.5306	483.6
0.3882	0.6764	316.8	0.3921	0.6521	421.2	0.2785	0.5779	519.5
0.5271	0.7085	328.8	0.5633	0.6983	443.4	0.3988	0.6306	555.8
0.6278	0.7291	334.2	0.6550	0.7234	449.7	0.6022	0.6939	587.2
0.7594	0.7675	337.7	0.7095	0.7428	452.2	0.7191	0.7365	595.0
0.8185	0.7932	338.1	0.7860	0.7740	452.7	0.7834	0.7683	595.3
0.8197	0.7951	337.7	0.8579	0.8148	448.6	0.9205	0.8735	574.1
0.8819	0.8357	333.4	0.9517	0.9115	428.6	0.9654	0.9343	554.8
0.9566	0.9181	319.7	1.0000	1.0000	404.6	1.0000	1.0000	530.6
1.0000	1.0000	302.4						

**Table 3.** Vapor pressure of pure compounds. Comparison between experimental data from present work and values calculated from literature;  $\Delta P\% = 100 \cdot (P - P_{tw}) / P_{tw}$ .

<i>T/K</i>		293.15		303.15		313.15	
<i>Fluid</i>	<i>Source</i>	<i>P/kPa</i>	$\Delta P\%$	<i>P/kPa</i>	$\Delta P\%$	<i>P/kPa</i>	$\Delta P\%$
HFC-245fa	This work (tw)	122.8		179.0		250.8	
	Sotani et al. [8]	126.0	2.63	181.5	1.41	254.3	1.40
	Mc Linden et al. [9]	123.8	0.81	179.0	0.00	251.8	0.40
HFC-134a	This work (tw)	571.3		769.4		1014.6	
	Baroncini et al. [10]	575.1	0.67	778.2	1.14	1029.8	1.50
	Wilson et al. [11]	571.6	0.05	770.1	0.09	1016.4	0.18
	Morrison et al. [12]	571.8	0.09	770.0	0.07	1016.1	0.15
	Baehr et al. [13]	571.8	0.09	770.2	0.10	1016.5	0.18
	Magee et al. [14]	570.0	-0.23	768.8	-0.07	1016.0	0.14
	Zhu et al. [15]	571.8	0.09	770.3	0.12	1016.3	0.17
	Kubota et al. [16]	572.1	0.15	770.1	0.09	1016.4	0.18
	Higashi [17]	568.2	-0.55	768.6	-0.10	1014.9	0.03
	Chung et al. [18]	570.9	-0.07	769.3	-0.01	1015.3	0.07
	Choi et al. [19]	570.8	-0.09	769.4	0.00	1017.6	0.30
	Mc Linden et al. [9]	571.7	0.07	770.2	0.10	1016.6	0.20
HC-600a	This work (tw)	302.4		404.6		530.6	
	Beattie et al. [20]	298.4	-1.31	399.6	-1.23	525.2	-1.02
	Parrish et al. [21]			408.0	0.84		
	Mc Linden et al. [9]	301.8	-0.20	404.4	-0.05	530.8	0.04

**Table 4.** Results of VLE data reduction using the RKS-HV EOS.

	<i>HFC-134a + HFC-245fa</i>			<i>HC-600a + HFC-245fa</i>		
<i>T/K</i>	293.15	303.15	313.15	293.15	303.15	313.15
<i>Bias</i> ( $\Delta P\%$ )	-0.0001	0.0000	-0.0002	0.0000	-0.0002	-0.0001
<i>AAD</i> ( $\Delta P\%$ )	0.0577	0.0260	0.0974	0.0602	0.0998	0.0732
<i>Bias</i> ( $\Delta y$ )	0.0033	0.0013	0.0023	0.0003	-0.0025	0.0002
<i>AAD</i> ( $\Delta y$ )	0.0033	0.0013	0.0023	0.0021	0.0025	0.0017

$$Bias(\Delta P\%) = \frac{100}{N_p} \sum_{i=1}^{N_p} \left( \frac{\Delta P}{P_{exp}} \right)_i ; \quad AAD(\Delta P\%) = \frac{100}{N_p} \sum_{i=1}^{N_p} \left( \frac{|\Delta P|}{P_{exp}} \right)_i$$

$$Bias(\Delta y) = \frac{1}{N_p} \sum_{i=1}^{N_p} (\Delta y)_i ; \quad AAD(\Delta y) = \frac{1}{N_p} \sum_{i=1}^{N_p} (|\Delta y|)_i$$

## FIGURE CAPTIONS

**Figure 1.** Vapor-liquid equilibrium for HFC-134a (1) + HFC-245fa (2) at  $T = 293.15$  K ( $\blacktriangle$ ),  $303.15$  ( $\diamond$ ) and  $313.15$  K ( $\bullet$ ); — RKS-HV EOS.

**Figure 2.** Vapor-liquid equilibrium for HC-600a (1) + HFC-245fa (2) at  $T = 293.15$  K ( $\blacktriangle$ ),  $303.15$  ( $\diamond$ ) and  $313.15$  K ( $\bullet$ ); — RKS-HV EOS.

**Figure 3.** Scatter diagram of saturated pressure deviations for HFC-134a (1) + HFC-245fa (2) at  $T = 293.15$  K ( $\blacktriangle$ ),  $303.15$  ( $\diamond$ ) and  $313.15$  K ( $\bullet$ ).

**Figure 4.** Scatter diagram of deviations in vapor phase composition for HFC-134a (1) + HFC-245fa (2) at  $T = 293.15$  K ( $\blacktriangle$ ),  $303.15$  ( $\diamond$ ) and  $313.15$  K ( $\bullet$ ).

**Figure 5.** Scatter diagram of saturated pressure deviations for HC-600a (1) + HFC-245fa (2) at  $T = 293.15$  K ( $\blacktriangle$ ),  $303.15$  ( $\diamond$ ) and  $313.15$  K ( $\bullet$ ).

**Figure 6.** Scatter diagram of deviations in vapor phase composition for HC-600a (1) + HFC-245fa (2) at  $T = 293.15$  K ( $\blacktriangle$ ),  $303.15$  ( $\diamond$ ) and  $313.15$  K ( $\bullet$ ).













